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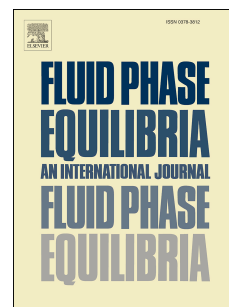
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# eCPA: An Ion-Specific Approach to Parametrization

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## Abstract

The eCPA equation of state has been shown to be a promising electrolyte model, for which several applications have been demonstrated. The model at its current status is, however, limited by the use of salt-specific parameters for the interactions between salts and water. Having salt-specific parameters limit the applicability to simple systems of ions, as it can only be applied when a common ion is found between the salts in the solution. For more complex systems of multiple ions/salts this may not work well. In this work the main goal is to eliminate this limitation by parametrizing the model with an ion-specific parameter set. The ion-specific parameters are estimated by a simultaneous fitting of parameters for 17 ions, consisting of 10 cations and 7 anions, and with data for 55 salts. The parameters are fitted to osmotic coefficient and mean ionic activity coefficient data in a wide temperature range from 273.15 K to above 500 K and up to an ionic strength of 6 molal. The parameters are found to yield similar deviations as the salt-specific parameters, however, for a few salts cation-anion interaction parameters were needed in order to obtain reasonable accuracy.

The parameters are applied to a series of systems, which include mixed salt osmotic coefficients, solid-liquid equilibrium and vapor-liquid equilibrium of water-methanol-salt, illustrating the applicability of the ion-specific parameters. Modelling of mixed salt osmotic coefficients illustrate that the parameters work well in salt mixtures, while the phase equilibria also illustrate the extension to mixed solvent systems.

**Keywords:** Equation of state, CPA, Debye-Hückel, Electrolytes, Parametrization

## 1. Introduction

Solutions containing electrolytes are present and important in many chemical processes. Whether it is waste water treatment, fertilizer productions, acid gas cleaning or many aspects of biochemical engineering, taking the electrolytes into account is key to understanding the processes [1]. Also in the petroleum industry salts and electrolytes play an important role, as salt has an effect on corrosion and scale formation in pipelines [1, 2]. Electrolyte content also has an effect on enhanced oil recovery [3]. Understanding these types of processes require knowledge about physical properties of the compounds in the system over a wide temperature and pressure range, in order to be able to do process design and optimization. Such information can be obtained through relevant experimental data, however, experimental data are expensive and difficult to obtain, and therefore there is a need for accurate thermodynamic models, that can rely on a limited amount of data to predict the relevant properties [4].

While electrolyte solutions have traditionally been modelled with activity coefficient models such as e-NRTL, Pitzer, MSE or Extended UNIQUAC [5, 6, 7, 8], and still are, in most process simulators, development of electrolyte equations of state (EoSs) have been extensive in the past decades. The typical approach is to base the model on an already existing EoS that can account

for the short range interactions. This could be a cubic EoS, as the extension to Peng-Robinson by Wu and Prausnitz [9], but also in many cases Statistical Associating Fluid Theory (SAFT) based EoSs [10, 11, 12], which are derived from statistical thermodynamics and also account for association. The Cubic Plus Association (CPA) EoS, which uses the attraction and repulsion interactions of the cubic EoS, Soave-Redlich-Kwong (SRK), but also accounts for association in a similar way to SAFT, has also been extended to electrolytes [13, 14, 15, 16, 17]. Most of these extensions rely on one of two models for the long range interaction between charged species; the Mean Spherical Approximation (MSA) [18] or the Debye-Hückel [19]. It has been shown by Maribo-Mogensen et al. that these two models perform similarly and that the static permittivity is a key parameter for obtaining accurate results with either of them [20].

While most of these models have a similar structure; an existing EoS extended with either MSA or Debye-Hückel, they are implemented in different ways. Some models utilize salt-specific parameters fitted for each salt [15, 21], however, strong electrolytes are typically assumed to be fully dissociated in water, and thus the actual compounds in the solutions are ions rather than salts. Therefore, most models utilize ion-specific parameters with a set of parameters for each ion [10, 11], and in a few implementations the ion-specific parameters are combined with one salt-specific parameter [12]. Besides the choice of salt- or ion-specific parameters, models also vary in terms of which parameters to treat as adjustable and what type of data to

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use to obtain these parameters. The number of adjustable parameters vary greatly, and while the type of parameters can be similar between models, they can be obtained in different ways. The ion diameter in the long range contribution, for example, is in some publications fixed to literature data values [11, 16], while in others it is treated as an adjustable parameter [10, 13]. Several property type data have been utilized in the parametrization of the models, e.g. in the works of Galindo et al. and Cameretti et al. [10, 11] the data used were density and vapor pressure. In more recent publications, including later publications from the two mentioned research groups, activity coefficient and/or osmotic coefficient data are widely used in parameter estimation [22, 23, 24, 25].

While many developments in electrolyte EoSs have been made in recent years, many of the developments are somewhat narrow in terms of application. For electrolyte EoSs to succeed and become as widely used as the well established activity coefficient models, there is a need for models with a wide range of applicability [4]. This means, that they must be parametrized for a wide range of ions, over a wider temperature range and that the model must be applicable to complex systems. Many of the models are either applied only to a limited number of ions and/or only at ambient temperatures, and often only applied to relatively simple systems [13, 14, 26].

The eCPA EoS presented by Maribo-Mogensen et al. could be a valid approach, as it has been applied to a large number of ions/salts over a wide temperature range and shown to work well for certain complex systems [16]. It utilises the Debye-Hückel equation for the long range interaction of the ions, as well as a Born term to account for ion solvation. One setback for the model is the form in which it is presented by Maribo-Mogensen et al. [16], i.e. the fact that it uses salt-specific interaction parameters for the interaction between salts and solvents. This limits the applicability to complex systems of ions, as it can only be applied when a common ion is found between the added salts in the solution, and for more complex systems of multiple ions/salts it may not work well.

One setback for the model in the form in which it is presented by Maribo-Mogensen et al. [16] is the fact that it uses salt-specific interaction parameters for the interaction between salts and solvents. This limits the applicability of the model, as it can only be applied when a common ion is found between the salts in the solution, and for more complex systems of multiple ions/salts this may not work well.

The aim of this work is to remove this limitation of the model by parametrizing it with an ion-specific approach, thus obtaining unique parameters for each ion instead of each salt. The system of ions that is investigated, is the same as the one modeled by Maribo-Mogensen et al. [16], consisting of 10 cations and 7 anions, using data for 55 salts, as this will yield a basis of comparison between the two approaches.

## 2. eCPA Equation of State

### 2.1. The Model

The electrolyte CPA (eCPA) EoS used in this work was proposed by Maribo-Mogensen et al. [16]. The model is based on

the CPA EoS [27] with a simplified radial distribution function [28] such that it, without the presence of ions, reduces to the CPA EoS. In addition to the CPA, additional terms are added to account for the long-range forces of the ions, such that the residual Helmholtz energy of an electrolyte system is calculated from:

$$A^r = A^{SRK} + A^{assoc} + A^{DH} + A^{Born} \quad (1)$$

The eCPA has the cubic SRK EoS as a base model [29] with the association term adopted from SAFT [30] added. In electrolyte solutions, the Debye-Hückel theory [19] and the Born model [31] are utilized to account for the electrostatic interactions. In both the Debye-Hückel and the Born terms the solvent is treated as a continuum described by the static permittivity of the solvent. In this work the static permittivity is described through the model by Maribo-Mogensen et al. [32], which is given by:

$$\frac{(2\varepsilon_r + \varepsilon_\infty)(\varepsilon_r + \varepsilon_\infty)}{\varepsilon_r} = \left( \frac{\varepsilon_\infty + 2}{3} \right)^2 \frac{N_A}{\varepsilon_0 k_B T v} \sum_i x_i g_i \mu_{i,0}^2 \quad (2)$$

In Eq. (2),  $\varepsilon_r$  is the static permittivity,  $\varepsilon_\infty$  is the infinite frequency permittivity obtained from the Clausius-Mossotti equation,  $\varepsilon_0$  is the vacuum permittivity,  $\mu_{i,0}$  is the dipole moment in vacuum, and finally,  $g_i$  is the Kirkwood g-factor given by:

$$g_i = 1 + \sum_j \frac{z_{ij} P_{ij} \cos \gamma_{ij} \mu_{0,j}}{P_i \cos \theta_{ij} + 1 \mu_{0,i}} \quad (3)$$

Here  $z_{ij}$  is the coordination number of molecule  $j$  around a central molecule  $i$ ,  $P_{ij}$  is the probability of molecule  $i$  being associated to molecule  $j$ , and  $\gamma_{ij}$  and  $\theta_{ij}$  represents the angles between the dipole moments of molecules  $i$  and  $j$ , and the angle between the hydrogen bonds of molecules  $i$  and  $j$ , respectively. This model for the static permittivity has been shown to yield accurate values for water and several organic solvents over an extended temperature and pressure range [32].

The eCPA utilises the Huron-Vidal infinite pressure mixing rule for the parameters describing the interaction between the ions and the solvents. The  $g^E$  model used is NRTL, which is simplified by defining the non-randomness parameter as zero, and assuming that it is symmetrical ( $\Delta U_{ij} = \Delta U_{ji}$ ). With these simplifications the mixing rule is:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g^{E,\infty}}{\ln 2} \quad (4)$$

$$\frac{g^{E,\infty}}{RT} = \frac{1}{b} \sum_i \sum_j x_i x_j b_j \frac{\Delta U_{ij}}{RT} \quad (5)$$

In these equations,  $\Delta U_{ij}$  is the ion-solvent interaction parameter, however, in order to use the model in a wide temperature range, a quadratic temperature dependence for this parameter is applied.

$$\frac{\Delta U_{ij}}{R} = \frac{\Delta U_{ij}^{ref}}{R} + \alpha_{ij} \left[ \left( 1 - \frac{T}{T_{\alpha,ij}} \right)^2 - \left( 1 - \frac{T_{ref}}{T_{\alpha,ij}} \right)^2 \right] \quad (6)$$

Here,  $\Delta U_{ij}^{ref}$ ,  $\alpha_{ij}$  and  $T_{\alpha,ij}$  are the three adjustable parameters of the temperature dependence between an ion,  $i$ , and a solvent,  $j$ .  $T_{ref}$  is the reference temperature at which the parameter  $\Delta U_{ij}^{ref}$  is valid. The mixing rule for the parameters describing the interaction between solvents and the ion-ion interactions are all still treated with Van der Waals 1 fluid mixing rules, as known from CPA [28].

## 2.2. Parametrization Approaches: Salt-specific vs. Ion-specific

In any type of modelling a key factor in getting accurate results is the parametrization of the model. In the work of Maribo-Mogensen et al. [16] the parametrization was salt-specific. The only adjustable parameters were the salt-solvent interaction parameters, as illustrated in Table 1. This salt-specific interaction parameter is then translated to ion parameters as an equal contribution to both ions in a salt. Having salt-specific parameters is convenient in terms of parametrization as the parameters are only dependent of one salt. This is illustrated in figure 1a where it is evident that for each pair of ions there is a parameter, thus NaCl has a parameter, NaBr has a parameter, and the two potassium salts have separate parameters as well. For single salt solutions this approach can be acceptable, however, in more complicated mixtures of salts, having these types of parameters can create problems. In a two salt solution with a common ion the salt-specific parameters would essentially imply two different values for the common ion parameter originating from each of the two salts. However, it can work, as it has been shown by Maribo-Mogensen et al. [16], by setting the value of the interaction parameter of the common ion to zero, and then calculate the contribution from the other two ions with Eq. (7).

$$\frac{\Delta U_{sw}}{RT} = \sum_{j \in s} \frac{v_j(b_j + b_w)}{v_s b_i + b_s} \frac{\Delta U_{jw}}{RT} \quad (7)$$

In Eq. (7)  $v_j$  is the stoichiometric number of ion  $j$  in salt,  $s$  here with water ( $w$ ) as a solvent.  $v_s$  is the total stoichiometric number of dissociated molecules in salt  $s$  and  $b_s$  is the co-volume parameter of the salt calculated from the ion co-volumes by  $b_s = \sum_{j \in s} v_j b_j$ . The main issue with salt-specific parameters occur when mixing two salts that have no common ions or when considering more complex multi-salt/ion systems. In the case of a mixture of NaCl and KBr, with reference to the example of Figure 1, the parameters from the two salts do not cross-interact, as the parameters of NaCl contributes to the sodium and the chloride ions and the KBr parameters contribute to the potassium and the bromide ions. However, assuming full dissociation, this mixture contains the same ions as a mixture of KCl and NaBr, which would yield different parameters for the given ions. Considering that a 1 molal - 1 molal NaCl - KBr mixture is identical to a 1 molal - 1 molal NaBr - KCl mixture, the use of salt-specific parameters is not consistent and viable.

The alternative to the salt-specific parametrization is an ion-specific parametrization. The model itself is ion-specific, e.g. all inputs for electrolytes are on ion basis, and thus having ion-specific parameters does seem like the "correct" way to parametrize the model. Having ion-specific parameters eliminates the issue with the salt-specific parameters with regards to

	Na <sup>+</sup>	K <sup>+</sup>
Cl <sup>-</sup>	$\Delta U_{NaCl-w}$	$\Delta U_{KCl-w}$
Br <sup>-</sup>	$\Delta U_{NaBr-w}$	$\Delta U_{KBr-w}$
(a) Salt-Specific		
	$\Delta U_{Na^+-w}$	$\Delta U_{K^+-w}$
$\Delta U_{Cl^- -w}$	NaCl	KCl
$\Delta U_{Br^- -w}$	NaBr	KBr
(b) Ion-Specific		

Figure 1: Illustration of the difference between salt-specific and ion-specific parameters, using the salt/ion-water interaction parameters as reference.

multi salt systems, as each ion will have its own unique parameter values, as illustrated in Figure 1b, and thus also eliminating the need for equations such as Eq. (7). Ion-specific parameters are, however, difficult to obtain, as the parameters of the cations are linked with those of the anions, and vice versa, as illustrated for a small system in Figure 1b. One parametrization approach for such systems is to fix the parameters of the hydrogen ion, H<sup>+</sup>, as a reference ion similar to Extended UNIQUAC [8]. Having fixed the hydrogen ion, the chloride ion, Cl<sup>-</sup>, parameters can then be estimated from HCl data. With fixed parameters for the chloride ion, the sodium ion, Na<sup>+</sup>, can then be fitted to NaCl data. This process can then be repeated with other ions through several different paths of salts, until all the ions in the system are parametrized. In this approach parameters are estimated to individual salt data which makes it fairly easy to parametrize, however, it also means that for most of the salts the results are predictions. In testing this approach with our model, it was found that these predictions are not very successful.

Table 1: Overview of the parameters used in the parameter estimation for both the Maribo-Mogensen et al. [16] salt-specific approach and the ion-specific approach of this work.  $\Gamma$  is the energy parameter of the SRK term ( $\Gamma = a_0/(Rb)$ ), with  $c_1$  being the temperature dependence,  $b$  is the co-volume,  $\epsilon_{A_i B_j}$  and  $\beta_{A_i B_j}$  are the association energy and association volume respectively,  $d_i$  is the ion diameter,  $R_{Born}$  is the Born radius, and  $\Delta U_{ref}$ ,  $\alpha$  and  $T_\alpha$  are the three parameters of the temperature dependence for the ion-water Huron-Vidal/NRTL mixing rule energy parameter.  $c_i$  is the Peneloux volume translation parameter

	Maribo-Mogensen et al. [16]	This Work
<u>SRK-term</u>		
$\Gamma$	0	Fit (ion)
$c_1$	0	0
$b$	$b = \frac{2}{3} N_A \pi d_i^3$ (ion)	
<u>Association-term</u>		
$\epsilon_{A_i B_j}$	0	0
$\beta_{A_i B_j}$	0	0
<u>Debye-Hückel-term</u>		
$d_i$	Literature (ion)	Fit (ion)
<u>Born-term</u>		
$R_{Born}$	adjusted to $\Delta H_{hyd}$ (ion)	
<u>Interaction Parameter</u>		
$\Delta U_{ref}$	Fit (salt)	Fit (ion)
$\alpha$	Fit (salt)	Fit (ion)
$T_\alpha$	Fit (salt)	Fit (ion)
<u>Volume Translation</u>		
$c_i$	Fit(salt)	Fit(ion)

	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	H <sup>+</sup>	Li <sup>+</sup>	Ca <sup>2+</sup>	Cs <sup>+</sup>	Rb <sup>+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
Cl <sup>-</sup>	1				3	5	7	8	9	10
Br <sup>-</sup>										
NO <sub>3</sub> <sup>-</sup>										
SO <sub>4</sub> <sup>2-</sup>										
OH <sup>-</sup>	2				3	5	7	8	9	10
I <sup>-</sup>	4									
F <sup>-</sup>	6					5	7	8	9	10

Figure 2: Illustration of the parametrization process, showing the order of addition of the ions to the parametrization, where 1 indicates the initial system, followed by the addition of 2, then 3, etc.

The approach used in this work is to use data for all salts in the system, and simultaneously estimate the ion parameters in the system. With this approach all simple salts are considered and the parameters will be determined to best fit many salts and not just a few. Adding ten cations and seven anions to such a parameter estimation requires a good initial estimate for the parameters in order to get as good an estimation as possible. In order to obtain as good an initial guess as possible, we start by parametrizing a smaller system of four cations and four anions. Such a system is less sensitive, and by using several initial guesses all converging to the same parameters it puts a higher confidence in the parameters. The system is then expanded with another ion, and all the parameters, including those estimated in the first estimation, are adjusted. Again several initial guesses for the new ion should converge to the same solution. This process is then repeated, every time adding a new ion, until all the ions of interest are added to the system. A final adjustment of all the parameters is then done. In Figure 2 this process is illustrated showing the initial system and the order in which the ions are added to the system.

### 2.3. eCPA Parameters

When modelling electrolyte solutions both solvent and ion parameters are important. The solvent parameters used in this work are existing CPA parameters, listed in Table 2. In this work the eCPA is parametrized for ions using the ion-specific approach described above, and its performances are compared to the performance of the salt-specific approach by Maribo-Mogensen et al. [16]. In order to get reasonable results with this ion-specific parametrization a few of the pure component parameters, that in the salt-specific approach were set zero or fixed to literature values, are now included in the parameter estimation. This is the case for the energy parameter in the SRK term ( $\Gamma$ ), and the size parameter in the Debye-Hückel term ( $d_i$ ), which are treated as adjustable parameters whereas they, in the salt-specific approach, were set to zero and a literature value re-

Table 2: CPA parameters for the solvents used in this work

	$b$ $\frac{\text{cm}^3}{\text{mol}}$	$\Gamma$ (K)	$c_1$	$\beta_{A_i B_j}$ $\cdot 10^3$	$\epsilon_{A_i B_j}$ (K)	Assoc. scheme	ref.
Water	14.52	1017.3	0.6736	69.2	2003.3	4C	[28]
Methanol	30.98	1573.7	0.4310	16.1	2957.8	2B	[28]

spectively, as seen in Table 1. In both approaches the co-volume parameter in the SRK term is calculated from the size parameter in the Debye-Hückel term, using the equation:  $b_0 = 2/3 N_A \pi d_i^3$ . This means that in this parametrization there are five truly adjustable parameters, within the model itself, for each ion. Two of the parameters are pure component and the other three are the temperature dependent interaction parameters between the ion and water.

The model parameters, both the pure component and the interactions, are estimated from osmotic coefficient and mean ionic activity coefficient data for salts in water, over a wide range of temperatures up to an ionic strength of 6 molal. Activity coefficient or osmotic coefficient are widely used data types for parametrization of electrolyte models [23, 24, 34], and were also the data used in the parametrization of Maribo-Mogensen et al. [16]. An overview of the data used in the parameter estimation is shown in Table 3, showing the number of datapoints for each salt, the temperature range and molality maximum. The parameters are estimated using the relative deviation of each data point with the objective function:

$$R = \sum_i \left( \frac{\gamma_{exp,i}^+ - \gamma_{calc,i}^+}{\gamma_{exp,i}^+} \right) w_i + \sum_i \left( \frac{\phi_{exp,i} - \phi_{calc,i}}{\phi_{exp,i}} \right) w_i \quad (8)$$

where *exp* and *calc* refers to experimental data and the eCPA calculation respectively. The  $w_i$  is a weight of each datapoint, which in this work is used to put even weight on each of the salts for which there are data. This is done by letting the weight follow:



Table 3: Overview of the data used for the parameter estimation,  $n_{dp}$  is the number of datapoints,  $n_{dp}@25^\circ\text{C}$  indicates how many of these datapoints are at  $25^\circ\text{C}$ ,  $m_{max}$  is the maximum molality of the data, and  $T_{min}$  and  $T_{max}$  are the minimum and the maximum temperature of the data. The density data are only at 298.15 K. All the data are for the salt in water, and all the data are found in the CERE electrolyte database [33]

Salts	$\Phi$					$\gamma^\pm$					$\rho$ $n_{dp}$
	$n_{dp}$	$n_{dp}$ @25°C	$m_{max}$ (molal)	$T_{min}$ (K)	$T_{max}$ (K)	$n_{dp}$	$n_{dp}$ @25°C	$m_{max}$ (molal)	$T_{min}$ (K)	$T_{max}$ (K)	
NaCl	939	222	6	273.15	473.15	727	53	6	273.15	523.15	554
NaBr	140	89	6	274.15	374.15	206	62	6	273.15	523.15	108
NaNO <sub>3</sub>	170	124	6	273.15	373.45	29	29	6	298.15	298.15	85
Na <sub>2</sub> SO <sub>4</sub>	231	95	2	273.15	498.15	93	39	2	273.15	498.15	143
NaOH	141	58	6	273.15	433.09	114	66	6	273.15	523.15	173
NaI	60	47	6	274.15	361.95	33	33	6	298.15	298.15	83
NaF	33	33	1	298.15	298.15	47	27	1	288.15	308.15	126
KCl	620	169	6	273.15	598.15	535	93	6	273.15	598.15	441
KBr	65	55	5.5	298.15	318.15	88	40	5	273.15	523.15	76
KNO <sub>3</sub>	180	133	6	274.15	348.15	24	24	3.5	298.15	298.15	143
K <sub>2</sub> SO <sub>4</sub>	157	64	2	273.15	498.15	85	31	2	273.15	498.15	100
KOH	143	58	6	293.15	433.09	85	37	6	273.15	523.15	40
KI	62	62	4.6	298.15	298.15	7	7	2	298.15	298.15	89
KF	56	31	6	276.55	357.33	29	29	6	298.15	298.15	52
MgCl <sub>2</sub>	172	99	2	298.15	473.15	67	37	2	273.15	523.15	333
MgBr <sub>2</sub>	41	37	2	273.15	323.15	44	44	2	298.15	298.2	49
Mg(NO <sub>3</sub> ) <sub>2</sub>	86	81	2	273.15	323.15	78	13	0.51	273.15	318.15	32
MgSO <sub>4</sub>	106	50	1.5	273.15	448.15	20	5	1.5	273.15	383.15	150
MgI <sub>2</sub>	39	39	2	298.15	298.15	32	32	2	298.15	298.15	16
HCl	52	52	6	298.15	298.15	361	90	6	273.15	548.15	171
HBr	85	73	6	273.15	323.15	108	53	6	278.15	398.15	21
HNO <sub>3</sub>	379	31	6	273.15	393.15	104	44	6	273.15	308.15	54
HI	52	52	6	298.15	298.15	29	29	6	298.15	298.15	16
LiCl	518	146	6	273.15	523.15	410	94	6	273.15	523.15	170
LiBr	112	74	6	273.15	373.45	95	47	6	273.15	523.15	50
LiNO <sub>3</sub>	181	109	6	273.15	523.15	50	29	6	298.15	523.15	49
Li <sub>2</sub> SO <sub>4</sub>	102	44	2	273.15	498.15	92	38	2	273.15	498.15	42
LiOH	133	76	5.68	293.15	443.09	96	48	5	273.15	523.15	16
LiI	92	72	4.99	298.15	343.15	23	23	3	298.15	298.15	20
CaCl <sub>2</sub>	278	163	2	273.15	445.4	76	38	2	288.15	343.15	419
CaBr <sub>2</sub>	35	35	2	298.15	298.15	104	59	2	278.15	318.15	49
Ca(NO <sub>3</sub> ) <sub>2</sub>	110	40	2	273.15	398.15	150	25	2	273.15	398.15	34
CaSO <sub>4</sub>	9	9	0.01	298.15	298.15	7	7	0.02	298.15	298.15	19
CaI <sub>2</sub>	44	41	2	273.15	298.15	38	38	1.92	298.15	298.15	16
CsCl	342	182	6	273.15	473.15	388	80	6	273.15	523.15	108
CsBr	62	62	5	298.15	298.15	83	35	5	273.15	523.15	50
CsNO <sub>3</sub>	48	39	3.28	278.15	323.15	19	19	1.5	298.15	298.15	33
Cs <sub>2</sub> SO <sub>4</sub>	59	19	2	298.15	498.15	76	36	2	298.15	498.15	24
CsOH	109	27	5.92	298.15	433.09	73	25	5	273.15	523.15	19
CsI	56	51	3.63	278.15	303.15	23	23	3	298.15	298.15	17
CsF	24	24	3.5	298.15	298.15	24	24	3.5	298.15	298.15	14
RbCl	95	95	6	298.15	298.15	29	29	6	298.15	298.15	107
RbBr	62	62	5	298.15	298.15	27	27	5	298.15	298.15	49
RbNO <sub>3</sub>	59	59	4.5	298.15	298.15	26	26	4.5	298.15	298.15	33
Rb <sub>2</sub> SO <sub>4</sub>	50	33	2	298.15	323.15	66	49	2	298.15	323.15	24
RbI	62	62	5	298.15	298.15	27	27	5	298.15	298.15	16
RbF	24	24	3.5	298.15	298.15	24	24	3.5	298.15	298.15	14
SrCl <sub>2</sub>	53	51	2	298.15	413.74	67	37	2	273.15	523.15	43
SrBr <sub>2</sub>	30	30	2	298.15	298.15	68	44	2	278.15	318.15	49
Sr(NO <sub>3</sub> ) <sub>2</sub>	15	15	2	298.15	298.15	78	13	0.51	273.15	318.15	22
SrI <sub>2</sub>	30	30	2	298.15	298.15	38	38	1.97	298.15	298.15	16
BaCl <sub>2</sub>	162	111	2	273.15	413.74	54	24	2	273.15	523.15	85
BaBr <sub>2</sub>	30	30	2	298.15	298.15	85	57	2	278.15	318.15	49
Ba(NO <sub>3</sub> ) <sub>2</sub>	8	8	0.4	298.15	298.15	60	10	0.2	273.15	318.15	11
BaI <sub>2</sub>	30	30	2	298.15	298.15	38	38	2	298.15	298.15	16

$$w_{i,j} = \frac{100}{n_{\gamma_j^+} + n_{\phi_j}} \quad (9)$$

Here  $w_{i,j}$  is the weight for a datapoint  $i$  for a salt  $j$ , and  $n$  is the number of datapoints for salt  $j$ . The exception from this is NaCl data which are weighted twice as high as the rest, thus still following Eq. 9 but multiplied by 2. This was introduced during the estimation process to maintain a good representation of this key salt. In the process of parameter estimation a few of the ion parameters got values that was not reasonable physically, with the  $T_\alpha$  and  $\alpha$  parameters going to extremes, e.g. a  $T_\alpha$  of several million. The occurrence of these extreme values is only found for both  $T_\alpha$  and  $\alpha$  simultaneously, and since for most ions the parameter values for  $T_\alpha$  is seen to be in the interval from 100 K to 1000 K, it was chosen to constrain the  $T_\alpha$  parameter to this range (100 K-1000 K). Similarly the size parameter was constrained to only positive values, however, no issues with negative values were seen prior to the constraints. The Born radius is adjusted to enthalpy of hydration at 25°C. This is similar to the approach by Maribo-Mogensen et al. [16]. The Born term provides the majority of the contribution to the enthalpy of hydration. Therefore it is found that adjusting the Born radius to this property is a good method. The adjustment of this parameter is done simultaneously with the other five adjustable parameters but optimized to match a single datapoint of enthalpy of hydration per salt.

The density is not included directly in the parameter estimation, and it was found that the model generally predicts the density to have a trend opposite to that of the experimental data. Therefore the density is matched by introducing a Peneloux volume translation, shown in Eq. 10.

$$v = v^{EoS} + \sum_i x_i c_i \quad (10)$$

Here  $v^{EoS}$  is the volume from the EoS,  $x_i$  is the mole fraction of ion  $i$ , and  $c_i$  is the Peneloux volume translation parameter for ion  $i$ . This volume translation parameter is estimated in a separate optimization, with the five parameters of the true model fixed at their final values. It is estimated for each ion using density data at 298.15 K, for all the salts investigated in this work, in a simultaneous estimation. An overview of the density data used are available in Table 3.

In Table 4 the pure component and ion-water interaction parameters are listed, these are estimated with the procedure described above. These parameters represent the system where all ten cations and seven anions are included in the estimation and are therefore the parameters of the final system considered. It should be noted that  $\sigma$ ,  $R_{Born}$ ,  $\Gamma$  and  $c$  are solvent independent parameters, while  $U_{ref}$ ,  $T_\alpha$  and  $\alpha$  are estimated for the water-ion interaction and are thus only valid for water-ion interactions. For other solvents the ion-solvent interaction parameters must be parametrized separately to those solvents.

### 3. Results and Discussion

The focus of this work was to determine an ion-specific parameter set for the eCPA model. With salt-specific parameters

the model cannot be extended to certain mixtures of ions, a limitation that ion-specific parameters eliminates. Furthermore the aim is to show that using an ion-specific approach could work well both for simple as well as complex systems. This is evaluated through simple aqueous solutions of single or mixed salt systems as well as extending to more complex mixtures and different types of phase equilibria. The results are typically listed as relative absolute deviations defined as:

$$RAD = \frac{1}{N_{dp}} \sum_i \left| \frac{x_i^{exp} - x_i^{calc}}{x_i^{exp}} \right| \quad (11)$$

Here  $N_{dp}$  is the number of datapoints, and  $x_i$  represents the property of interest. Superscripts *exp* and *calc* represent experimental data and calculated results with the model respectively.

#### 3.1. Single Salt Aqueous Solutions

In the parameter estimation process we have considered a system of 17 ions consisting of 10 cations and 7 anions and correlated activity coefficients, osmotic coefficients and densities for 55 binary salt-water systems. The deviations from the data listed in Table 3 are shown in Table 5, where deviations using the salt-specific approach of Maribo-Mogensen et al. [16] are also provided for comparison. The overall difference in deviation between the salt-specific parameters and the ion-specific parameters is on average approximately 1 percentage point for both of the data types; osmotic coefficient and mean ionic activity coefficient. For around two-thirds of the salts the deviations are higher with the ion-specific parameters than with the salt-specific parameters. For most systems, the deviations are slightly higher, but for a few the difference is 5-6 percentage points. The deviations for the remaining third of the salts are lowest with the ion-specific parameter set. For most of the salt also only slightly, but for a few with up to approx. 5 percentage points for activity coefficient and approx. 3 percentage points for osmotic coefficient.

Based on these observed deviations it was clear that while these ion-specific parameters result in acceptable deviations for most of the salts there are a few salts with high deviations, especially compared to the deviations with the salt-specific approach. This is the case for instance for  $\text{Na}_2\text{SO}_4$ , for which the deviations with the ion-specific parameters are significantly higher than with the salt-specific approach, 9.4% vs. 2.1% with regards to osmotic coefficient. A similar difference is seen for a few of the other salts, and therefore it was decided to introduce parameters for the interactions between anions and cations. These interaction parameters are estimated from the same data, with the same objective function, Eq. 8, individually for each of the cation-anion pairs. It was found that for 20 of the cation-anion pairs a non-zero interaction parameter could improve the description. For  $\text{Na}_2\text{SO}_4$  a  $k_{ij}$  of -0.4847 eliminates the big difference in deviation between salt-specific and ion-specific parameters, with the deviation for osmotic coefficient now being 2.5%, which is much closer to the salt-specific value. The difference in performance when including the  $k_{ij}$  for  $\text{Na}_2\text{SO}_4$  is illustrated in Figure 3 where the osmotic coefficient of  $\text{Na}_2\text{SO}_4$  is presented with and without the use of the



Table 4: Ion-specific parameters determined in this work, using the procedure described. Here  $\sigma$ ,  $R_{Born}$ ,  $\Gamma$  and  $c$  are solvent independent, while  $U_{ref}$ ,  $T_a$  and  $\alpha$  are estimated for the water-ion interaction and are thus only valid for water-ion interactions.

ions	$\sigma$ (Å)	$R_{Born}$ (Å)	$U_{ref,wi}$ (K)	$T_{a,wi}$ (K)	$\alpha_{wi}$ (K)	$\Gamma$ (K)	Peneloux $c$ (cm <sup>3</sup> /mol)
Na <sup>+</sup>	2.63	1.54	91.46	260.75	1449.01	959.54	-36.17
K <sup>+</sup>	2.90	2.04	53.57	999.89	-2770.48	571.37	-36.55
Mg <sup>2+</sup>	3.42	1.46	440.04	102.49	207.42	4935.39	-75.65
H <sup>+</sup>	0.18	0.62	9.87	336.64	482.52	887.90	-4.31
Li <sup>+</sup>	2.28	1.36	6.66	100.21	141.80	3059.73	-22.81
Ca <sup>2+</sup>	1.17	1.73	595.83	492.90	376.77	6261.18	-24.22
Cs <sup>+</sup>	3.96	2.69	0.002	932.42	-1402.36	2207.29	-78.77
Rb <sup>+</sup>	3.31	2.72	-0.0004	315.70	-23764.91	1434.74	-48.71
Sr <sup>2+</sup>	2.88	1.89	1.05	158.18	546.29	642.30	-52.21
Ba <sup>2+</sup>	1.81	2.09	-532.15	469.72	-6616.16	2514.53	-23.68
Cl <sup>-</sup>	3.57	1.99	-220.22	413.07	1579.19	1878.78	-39.17
Br <sup>-</sup>	3.84	2.17	-221.79	435.89	1693.81	1338.81	-51.56
NO <sub>3</sub> <sup>-</sup>	3.81	2.43	-1.68	259.17	-71.67	96.46	-48.04
SO <sub>4</sub> <sup>2-</sup>	3.14	2.40	0.67	433.55	5391.99	2903.63	-0.85
OH <sup>-</sup>	3.06	1.51	0.20	363.10	3252.16	9660.11	-14.85
I <sup>-</sup>	4.20	2.23	-217.72	425.28	2480.95	1900.80	-63.37
F <sup>-</sup>	3.54	1.12	-5.84	319.98	24249.67	0.00	-51.82

$k_{ij}$ . From this it is also clear that the fit and the trends are greatly improved, and when using the  $k_{ij}$ , the ion-specific parameters behave close to the salt-specific ones. The  $k_{ij}$  values found are listed in Table 5, along with the deviations to osmotic coefficient and activity coefficient. For all the ion-ion interactions where no  $k_{ij}$  is listed, the interaction parameter found in the optimizations are either zero, or very close to zero ( $10^{-3}$ ) and yielding no improvements to the deviations. Hence it was decided to set the interaction parameter to zero. Most of the 20 ion-ion pairs, for which interaction parameters are found, slightly improve already acceptable deviations, but for the few problematic cases, such as the already described Na<sub>2</sub>SO<sub>4</sub>, and Cs<sub>2</sub>SO<sub>4</sub> the improvements in deviations are significant. When including the  $k_{ij}$ s, the average deviations for all the salts are naturally lowered as well, the average deviation are still not on the level of the salt-specific parameters, however, the difference is small and within half of a percentage point.

When having applied  $k_{ij}$  between 20 of the cation-anion pairs, (were for the remaining salts no improvements are found with  $k_{ij}$ s) it is of interest to investigate if there is a general trend, e.g. if all the sulphate interactions have a similar parameter. If for all sulphate interactions a similar  $k_{ij}$  is found, it could be an indication for wrong pure component sulphate parameters. When examining the ion-ion interaction parameters it is clear that three of the ions; the hydrogen, magnesium and the fluoride ions, do not have a single ion-ion interaction parameter different from zero, while the remaining ions in the system have at least one ion-ion interaction parameter different from zero. Four of the ions stand out, having four or five interactions with other ions that are non-zero; this is the case for the sodium ion, the chloride ion, the bromide ion and the sulphate ion. Applying an ion-ion interaction parameter improves the accuracy for sodium salts in five out of the seven sodium salts investigated. For four of these, the  $k_{ij}$  needed to improve the deviations is positive, however, for Na<sub>2</sub>SO<sub>4</sub> a large negative  $k_{ij}$  is needed. The four sulphate salts, for which a non-zero ion-ion interac-

tion parameter is found, do not follow any clear trend either, for Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> the  $k_{ij}$ s are large negative values, while for Li<sub>2</sub>SO<sub>4</sub> and Cs<sub>2</sub>SO<sub>4</sub> the  $k_{ij}$ s are positive. Overall there is not found any trends in the ion-ion interaction parameters that would suggest that pure component or ion-water interaction parameters are systematically wrong.

For many of the salts investigated, the deviation with the salt-specific and the ion-specific parameters are very similar, as it is for NaCl where the difference in deviation is very small. In Figure 4(a) the mean ionic activity coefficient for NaCl is shown, and it can be seen that while the deviations listed are very similar, the behaviour is slightly different. The ion-specific parameters result in a more accurate description at 298.15 K capturing the minimum value in activity coefficient better. At

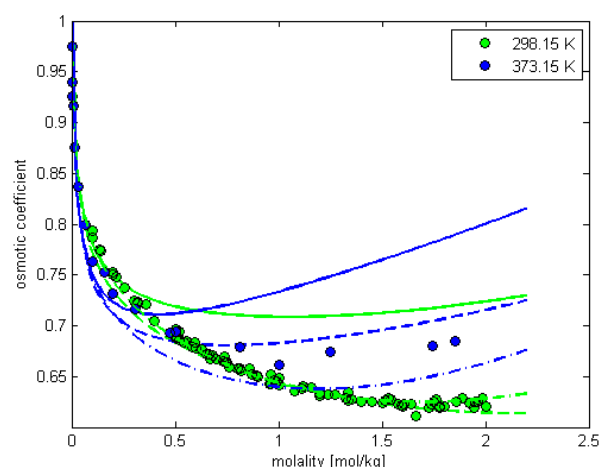


Figure 3: Osmotic coefficient of Na<sub>2</sub>SO<sub>4</sub>. The solid lines are with the parameters of this work without the ion-ion  $k_{ij}$ , the dashed lines are with the parameters of this work including the ion-ion  $k_{ij}$  and the dash-dot lines are using the salt-specific parameters of Maribo-Mogensen et al. [16].

Table 5: Deviations from activity coefficients, osmotic coefficients and density, with salt-specific parameters of Maribo-Mogensen et al.[16], with the ion-specific parameters of this work (without  $k_{ij}$ ) and with the ion-specific parameters of this work with the  $k_{ij}$  between anion and cation. The  $k_{ij}$  used is listed.

Salt	Maribo-Mogensen et al.			This work			$k_{ij}$	This Work + $k_{ij}$		
	$\gamma^{\pm}$ RAD (%)	$\Phi$ RAD (%)	$\rho$ RAD (%)	$\gamma^{\pm}$ RAD (%)	$\Phi$ RAD (%)	$\rho$ RAD (%)		$\gamma^{\pm}$ RAD (%)	$\Phi$ RAD (%)	$\rho$ RAD (%)
NaCl	2.37	1.48	0.73	2.58	1.28	0.71	-	2.58	1.28	0.71
NaBr	7.54	2.39	0.73	5.46	2.42	0.67	0.184	3.70	1.91	0.67
NaNO <sub>3</sub>	3.71	2.12	0.65	6.51	6.1	0.76	0.1772	5.77	6.03	0.76
Na <sub>2</sub> SO <sub>4</sub>	3.71	2.06	4.59	6.96	9.37	0.75	-0.4847	4.69	2.53	0.75
NaOH	4.14	1.87	0.78	7.51	2.68	1.65	0.1188	3.69	2.32	1.65
NaI	5.8	3.56	0.74	5.27	4.39	0.68	0.2653	2.72	3.38	0.68
NaF	2.23	1.01	0.81	5.04	4.37	0.75	-	5.04	4.37	0.75
KCl	3.48	1.83	0.7	6.7	3.86	0.76	-	6.7	3.86	0.76
KBr	4.93	0.7	0.75	4.3	0.83	0.67	-	4.30	0.83	0.67
KNO <sub>3</sub>	0.43	2.94	0.84	2.13	5.52	0.74	-	2.13	5.52	0.74
K <sub>2</sub> SO <sub>4</sub>	3.06	1.82	2.92	5.64	4.27	0.86	-0.43	3.39	1.62	0.86
KOH	5.7	1.9	0.76	5.56	2.61	0.83	0.1402	3.39	2.27	0.83
KI	1.59	1.14	0.73	0.56	0.46	0.7	-	0.56	0.46	0.7
KF	1.51	1.72	0.65	4.01	7.12	0.42	-	4.01	7.12	0.42
MgCl <sub>2</sub>	11.89	4.73	4.75	7.06	3.36	1.06	-	7.06	3.36	1.06
MgBr <sub>2</sub>	9.42	3.61	4.99	6.89	1.8	0.32	-	6.89	1.8	0.32
Mg(NO <sub>3</sub> ) <sub>2</sub>	7.87	2.66	1.63	5.93	4.14	0.89	-	5.93	4.14	0.89
MgSO <sub>4</sub>	7.94	7.81	0.79	3.64	4.86	0.84	-	3.64	4.86	0.84
MgI <sub>2</sub>	4.52	3.61	1.86	1.94	1.69	0.58	-	1.94	1.64	0.58
HCl	4.08	1.52	0.74	6.5	2.83	0.66	-	6.5	2.83	0.66
HBr	3.88	11.58	0.59	4.22	12.49	0.52	-	4.22	12.49	0.52
HNO <sub>3</sub>	5.11	6.1	0.79	4.74	3.49	0.66	-	4.74	3.49	0.66
HI	4.34	8.51	0.81	8.18	9.99	0.57	-	8.18	9.99	0.57
LiCl	5.74	3.02	0.76	10.36	4.22	0.71	0.2193	8.14	3.43	0.72
LiBr	7.56	5.5	0.98	8.2	5.58	0.49	-	8.2	5.58	0.49
LiNO <sub>3</sub>	3.21	3.69	0.68	4.81	3.95	0.59	-	4.81	3.95	0.59
Li <sub>2</sub> SO <sub>4</sub>	3.81	2.96	4.84	10.66	5.14	0.48	0.2750	5.59	3.60	0.49
LiOH	2.92	1.69	0.57	6.33	6.06	0.84	-	6.33	6.06	0.84
LiI	1.84	2.6	0.96	7	3.69	1.01	-0.1904	2.16	2.79	0.99
CaCl <sub>2</sub>	4.89	5.17	6.91	9.68	5	0.64	0.4090	8.42	3.90	0.66
CaBr <sub>2</sub>	12.73	2.13	5.19	14.13	3.01	0.87	-	14.13	3.01	0.87
Ca(NO <sub>3</sub> ) <sub>2</sub>	9.42	3.72	2.61	12.36	5.31	0.71	-	12.36	5.31	0.71
CaSO <sub>4</sub>	13.83	3.51	0.76	10.68	1.6	0.8	-	10.68	1.6	0.80
CaI <sub>2</sub>	5.74	3.19	2.07	6.8	4.81	2.03	-0.1009	6.59	4.68	2.05
CsCl	3.66	1.44	0.64	7.63	4.16	0.5	0.0244	7.55	3.92	0.51
CsBr	5.04	2.16	0.87	5.38	1.71	0.32	-	5.38	1.71	0.32
CsNO <sub>3</sub>	0.95	11.89	0.84	5.03	10.18	0.39	-	5.03	10.18	0.39
Cs <sub>2</sub> SO <sub>4</sub>	2.16	1.95	10.16	6.73	6.55	1.04	0.2156	2.71	3.21	0.95
CsOH	6.02	1.97	0.8	8.3	2.85	0.5	-	8.3	2.85	0.5
CsI	3.48	1.27	0.86	3.97	1.38	0.96	-0.0353	2.26	1.66	0.94
CsF	0.87	0.6	0.73	6.36	2.62	0.32	-	6.36	2.62	0.32
RbCl	1.78	0.81	0.66	1.66	1.18	0.55	-	1.66	1.18	0.55
RbBr	-	-	-	4.13	1.17	0.37	-0.0675	2.09	1.36	0.35
RbNO <sub>3</sub>	1.35	0.68	0.88	1.55	1.91	1.03	0.1765	1.24	1.42	1.04
Rb <sub>2</sub> SO <sub>4</sub>	1.87	1.38	9.67	1.54	1.63	0.32	-	1.54	1.63	0.32
RbI	-	-	-	6.59	1.79	0.94	-0.0927	2.94	1.95	0.92
RbF	2.6	0.95	0.72	3.85	2	0.34	-	3.85	2	0.34
SrCl <sub>2</sub>	6.1	4.66	3.45	5.45	5.19	1.69	-0.2490	4.55	2.96	1.69
SrBr <sub>2</sub>	4.65	3.23	6.25	3.73	2.6	1.01	-	3.73	2.6	1.01
Sr(NO <sub>3</sub> ) <sub>2</sub>	7.24	3.7	2.26	4.94	6.03	1.02	-	4.94	6.03	1.02
SrI <sub>2</sub>	4.31	3.84	1.99	4.01	2.57	0.81	-	4.01	2.57	0.81
BaCl <sub>2</sub>	8.98	2.12	3.28	9.4	6.4	0.79	-	9.4	6.4	0.79
BaBr <sub>2</sub>	3.15	2.83	6.22	5.12	5.71	1.12	-0.1854	4.57	4.36	1.09
Ba(NO <sub>3</sub> ) <sub>2</sub>	3.12	3.11	0.78	2.9	9.35	0.76	-	2.9	9.35	0.76
BaI <sub>2</sub>	3.45	3.35	2.12	5.45	3.58	0.65	-	5.45	3.58	0.65
average	4.75	3.13	2.13	5.86	4.16	0.76		5.08	3.74	0.76

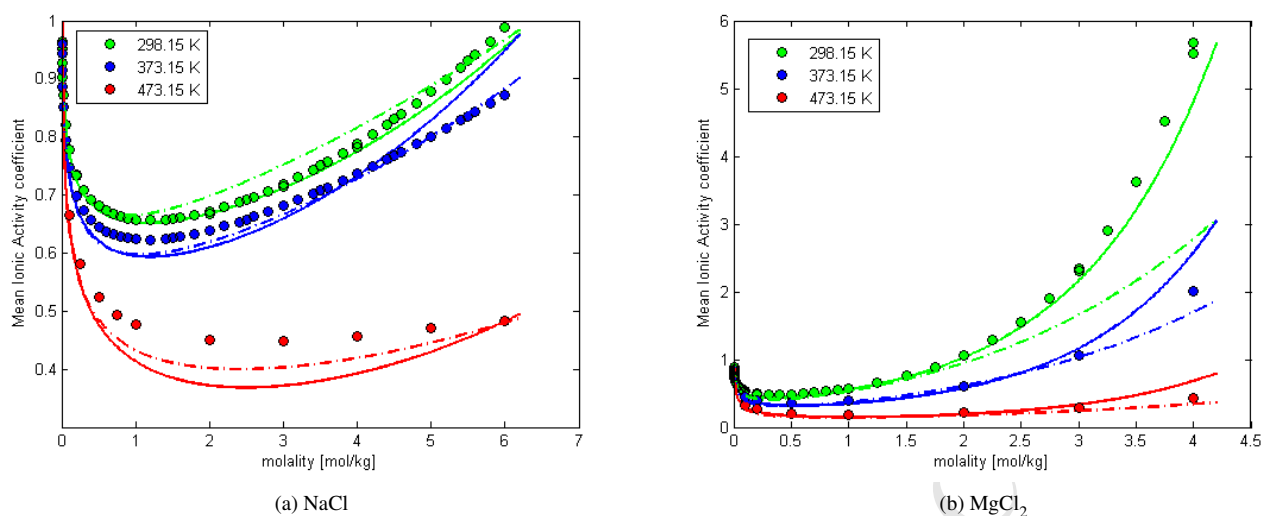


Figure 4: Mean ionic activity coefficient of (a) NaCl and (b)  $\text{MgCl}_2$ . The solid lines are with the parameters of this work and the dash-dot line using the salt-specific parameters of Maribo-Mogensen et al. [16].

373.15 K, however, while both parameter sets fail to capture the minimum, the salt-specific parameters are more accurate and follow the trend of the data better. The same is observed at 473.15 K. For  $\text{MgCl}_2$  the opposite is observed. In terms of deviations, for the mean ionic activity coefficient, the ion-specific parameters yield a lower value than when using salt-specific parameters, however, while the ion-specific parameters are more accurate, the behaviour in the range of the data (ionic strength of 6 molal) seems similar. The significant difference in deviation, between the two parametrizations is mainly due to the fact, that at high temperatures the value of the activity coefficient is very low, thus even small absolute deviations will yield higher relative deviations. In Figure 4(b), where the mean ionic activity coefficient is shown up to an ionic strength of 12 molal, the behaviour between the two parametrizations is very different. The ion-specific parameters extrapolate well beyond the ionic strength limit of the data in the parameter estimation of 6 molal, and predict accurately the increase in the activity coefficient at high molalities at 298.15 K, while the salt-specific parameters do not. At higher temperatures, however, this increase in activity coefficient at high molalities is overestimated with the ion-specific parameters but is underestimated with the salt-specific parameters.

When looking at the correlation of the density using the Peneloux volume translation, it is clear from the deviations in Table 5 that we are very successful at correlating the density at 298.15 K, as the ion-specific parameters show a deviation on average of 0.7%, and almost all of the salts have below 1% deviation. In the estimation only data at 298.15 K were used as the parameter is temperature independent and data at that temperature were available for all salts. The density prediction at higher temperatures is shown in figure 5, where the density of a NaCl solution is presented at three different temperatures. As expected, the correlation at 298.15 K is very accurate, however, underestimation is seen at higher temperatures. The prediction

at higher temperatures is still much better than without the volume correction where it is observed that the density will decrease when going towards higher molalities of salt, which is clearly a wrong trend. If very accurate density at high temperatures is needed, one possible solution for the higher deviations at higher temperatures will be to introduce a temperature dependent volume correction. Such a temperature dependence would most likely be linear and thus include one additional parameter to the model.

### 3.2. Mixed Salt Osmotic Coefficients

The main issue with the salt-specific parameters of Maribo-Mogensen et al. [16] is its applicability to mixtures. While some mixtures with common ions such as NaCl-KCl can be

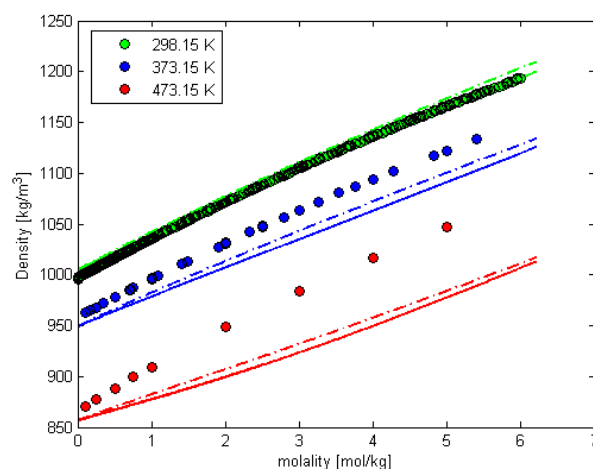


Figure 5: Density of NaCl. The solid lines are with the parameters of this work and the dash-dot lines using the salt-specific parameters of Maribo-Mogensen et al. [16].

Table 6: Deviations from osmotic coefficient data for mixed salt systems, modelled with ion-specific parameters including the use of the ion-ion interaction parameter. All data are from [33].

Mixture	Temperature (K)	RAD (%)
NaCl-KCl	298.15-313.15	2.73
NaCl-CaCl <sub>2</sub>	381.15-413.15	3.41
NaCl-LiCl	298.15	4.56
NaCl-CsCl	298.15	7.96
NaCl-MgCl <sub>2</sub>	298.15	1.03
KCl-CaCl <sub>2</sub>	298.15	5.29
LiCl-BaCl <sub>2</sub>	298.15	3.86
NaCl-KBr	298.15	1.59
NaCl-MgSO <sub>4</sub>	298.15	4.46
Na <sub>2</sub> SO <sub>4</sub> -MgCl <sub>2</sub>	298.15	1.11
NaNO <sub>3</sub> -LiNO <sub>3</sub>	298.15	5.48
KNO <sub>3</sub> -Mg(NO <sub>3</sub> ) <sub>2</sub>	298.15	2.19
K <sub>2</sub> SO <sub>4</sub> -MgSO <sub>4</sub>	298.15	6.68
Average		3.98

modelled with the salt-specific parameters, there will be problems when no common ions are present as for instance in a mixture of Na<sub>2</sub>SO<sub>4</sub>-MgCl<sub>2</sub>, as discussed in section 2.2. We have applied our new ion-specific parameters to a number of salt mixtures to investigate the model and parameters' ability to predict the osmotic coefficient of mixed salt systems. Most of the mixed salt data for osmotic coefficient found are at 298.15 K, however, a few high temperature data are also included. The RAD for these calculations are presented in Table 6. The deviations found correspond well with the deviations found for the individual salts, and while only having a single high temperature case that is also predicted accurately. Two mixtures of particular interest are the MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>-water and the NaCl-MgSO<sub>4</sub>-water mixtures. These two mixtures are made by dissolving two different sets of salts, however, the ions in the solution are the same, and a 1 molal MgCl<sub>2</sub>- 1 molal Na<sub>2</sub>SO<sub>4</sub> solution is identical to a 1 molal MgSO<sub>4</sub> - 2 molal NaCl solution under the assumption of full dissociation. While the deviation for the two systems is acceptable, there is a clear difference as the former has a deviation of 1.1% and the latter has a deviation of 4.5%. This could be due to variance in the data, but as the two datasets originate from the same publication [35] it is clear that they were measured with the same procedure. Upon a more thorough investigation of the individual datapoints, the main reason for the NaCl-MgSO<sub>4</sub>-water system having higher deviation than the MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>-water system, is that a high proportion of the data is dominated by MgSO<sub>4</sub>. The single salt, MgSO<sub>4</sub>-water osmotic coefficient deviation is acceptable at 4.9%, however, there is a range around the minimum in osmotic coefficient where the performance is less accurate, and for the NaCl-MgSO<sub>4</sub>-water mixture many of the datapoints fall within this same range. Based on the two different solutions it seems that for this four ion system the least accurate descriptions will be found when there is a high proportion of the magnesium and sulphate ions.

### 3.3. Solid Liquid Equilibrium

Salt solubility is another important property for electrolyte solutions. When modelling salt solubility, one relies not only on the EoS, but also on the equilibrium constant for the solids. The equilibrium equation solved for the solid-liquid equilibrium (SLE) is given as:

$$\ln K_s = RT \sum_i v_{i,s} \ln a_i \quad (12)$$

Here  $a_i$  is the component activity and  $K_s$  is the equilibrium constant calculated based on the standard state properties: standard state Gibbs energy of formation, standard state enthalpy of formation and standard state heat capacity. In the work of Schlaikjer et al. [17] a thorough description and investigation of eCPA applied to solid-liquid equilibrium is presented using salt-specific parameters. The standard state properties are, for some salts, available from Wagman et al. [36], however, for most hydrated salts these standard state properties are not available. In the work of Schlaikjer et al. [17] these standard state properties were adjusted along with the model parameters in an effort to correlate accurate salt solubility in an extended temperature range. The new ion-specific parameters of the current work are not estimated to solubility data, and thus when calculating salt solubility the model parameters are fixed. From the work of Schlaikjer et al. it was evident that adjustments of the standard state properties were very important for the models ability to accurately calculate solubility. It is found that the standard state properties can be adjusted such that accurate solubility can be obtained with the parameters of this work, when using an approach similar to that used in Schlaikjer et al. [17] for adjusting the standard state properties not available from Wagman et al. [36]. In Figure 6 the solubility of NaCl is presented after the adjustment of the standard state properties of the solid salts, using the ion-specific parameter of this work. It presents two different solutions, one where only standard state properties of the hydrated NaCl 2 H<sub>2</sub>O are adjusted while the standard state properties of NaCl are kept constant (at literature values) and one where the standard state properties of both salts were adjusted in order to investigate if accurate solubility could be correlated. This shows that while relatively accurate calculations at lower temperatures can be found, when only adjusting the hydrated salt, very accurate correlations can be found in the full temperature range only if the standard state properties of both salts were adjusted. The standard state properties used in this work are presented in Table 7, and comparing the literature values for NaCl with the adjusted ones show that the system is relatively sensitive and a 1% change is what makes the difference. While, from a theoretical point of view, the correct approach will be to keep the literature values when available. From a practical and engineering point of view correlating the standard states would be useful, and considering the relatively small changes needed, this is not a completely unreasonable approach.

Having accurately determined the solubility of NaCl which has a relatively simple solubility profile, the solubility of other salts with more complex solubility profiles are investigated. In

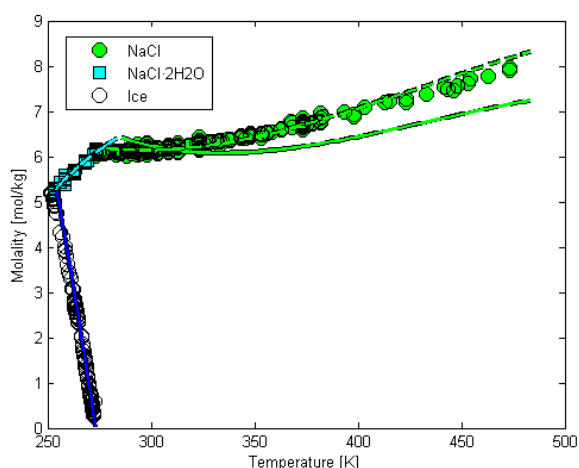


Figure 6: Freezing point depression and solubility of NaCl in water modelled with the ion-specific parameters of this work. The solid line represents results where the standard state properties are adjusted only for NaCl 2 H<sub>2</sub>O, and the dashed line where the standard state properties of both salts are adjusted.

Figure 7 the solubility of MgCl<sub>2</sub> and MgSO<sub>4</sub> are presented. Again the standard state properties are adjusted and the correlation for both salts is successful over the entire temperature range of the data. The only part of the solubility profile that the model does not accurately calculate is at low temperatures for MgCl<sub>2</sub>, in the range where the salt will precipitate as MgCl<sub>2</sub> 8 H<sub>2</sub>O. This small part cannot be matched without adjusting the model parameters, however, the deviation is not substantial. The correlation of solubility for these two salts clearly demonstrates the model's ability to calculate solubility and that these calculations depend greatly on the standard state properties.

The salt-specific parameters of Maribo-Mogensen et al. were applied to the mixed salt system of NaCl, Na<sub>2</sub>SO<sub>4</sub>, water and methanol [16]. In Figure 8 the same system is shown using the ion-specific parameters of this work. In this system the methanol parameters shown in Table 2 are used, along with a water-methanol interaction parameter of -0.09 [37]. Salt-specific interaction parameters between NaCl and methanol, and Na<sub>2</sub>SO<sub>4</sub> and methanol are adjusted directly to the SLE system since determining ion-specific parameters for such a system with a limited amount of data will not result in trustworthy results. The salt-methanol interaction parameters found are listed in Table 8. It is seen from Figure 8 that the methanol free system is predicted well. For the calculation with methanol in the system the part that precipitates as NaCl and Na<sub>2</sub>SO<sub>4</sub> are acceptable and show correct trends. For the precipitation of Na<sub>2</sub>SO<sub>4</sub> 10 H<sub>2</sub>O the picture is not as clear. At low methanol content the precipitation at zero NaCl content is accurate, however, the solubility is overestimated when more NaCl is added to the mixture. At a higher methanol content on the other hand, the Na<sub>2</sub>SO<sub>4</sub> 10 H<sub>2</sub>O solubility is underestimated. This corresponds well with what was observed with the salt-specific parameter by Maribo-Mogensen et al. where the same type of behaviour was observed.

Table 7: Standard state properties of solid salts used in this work. The NaCl/NaCl 2 H<sub>2</sub>O system marked with (1) is with NaCl having literature values, and the system marked (2) is with fitted values for NaCl also.

	$\Delta_{form}G$ (kJ/mol)	$\Delta_{form}H$ (kJ/mol)	$C_p^0$ /J/(mol·K)
NaCl (1)	-384.1	-411.2	50.5
NaCl 2 H <sub>2</sub> O (1)	-859.2	-994.3	230.1
NaCl (2)	-384.3	-415.3	50.5
NaCl 2 H <sub>2</sub> O (2)	-859.2	-994.3	230.1
Na <sub>2</sub> SO <sub>4</sub>	-1270.6	-1393.0	128.2
Na <sub>2</sub> SO <sub>4</sub> 10 H <sub>2</sub> O	-3647.1	-4321.9	492.2
MgCl <sub>2</sub> 2 H <sub>2</sub> O	-1152.4	-1460.7	151.4
MgCl <sub>2</sub> 4 H <sub>2</sub> O	-1635.1	-1975.6	231.4
MgCl <sub>2</sub> 6 H <sub>2</sub> O	-2115.7	-2519.2	311.4
MgCl <sub>2</sub> 8 H <sub>2</sub> O	-2592.8	-3108.1	391.4
MgCl <sub>2</sub> 12 H <sub>2</sub> O	-3545.7	-4272.4	551.4
MgSO <sub>4</sub> H <sub>2</sub> O	-1434.9	-1610.3	98.1
MgSO <sub>4</sub> 6 H <sub>2</sub> O	-2632.1	-3100.4	421.2
MgSO <sub>4</sub> 7 H <sub>2</sub> O	-2870.2	-3391.2	247.5
MgSO <sub>4</sub> 12 H <sub>2</sub> O	-4056.0	-4827.7	576.0

Table 8:  $\Delta U_{meOH-salt}$  interaction parameter

	NaCl	Na <sub>2</sub> SO <sub>4</sub>	KCl	NaBr	LiCl	NaF
$\Delta U$ (K)	825	1182	1120	642	608	1560

### 3.4. Vapor Liquid Equilibrium

Having applied the model to mixed solvent solubility in the previous section, it is also of interest to apply the model to other types of phase equilibrium. Keeping methanol as the other solvent we have applied the model to vapor-liquid equilibrium (VLE) for four different mixtures. As with the solubility in mixed solvents there is a need for salt/ion- methanol interaction parameters, and also here it is decided to use salt-specific interaction parameters for interaction, due to the fact that data are scarce and typically at low temperatures. A single temperature independent salt-methanol interaction parameter is fitted for each salt-methanol system, and the parameter is adjusted directly to the VLE data. In Figure 9 four isobaric VLE plots of water-methanol-salt are presented with four different salts. The data are given with fixed salt molalities, which are given with respect to water. This means that at the pure methanol limit of the phase diagram the solution is considered as salt free. The content of salt in the pure water should increase the boiling point of the solution, and this is also what is observed with the model. The highest increase in boiling point is seen with the NaBr and LiCl solutions, which is expected, as these two solutions also have the highest molalities of the four at 4 molal. Both the dew point and the bubble point curves are calculated accurately in all four cases, and it is fair to state that the salt induced changes to the VLE are captured by the model.



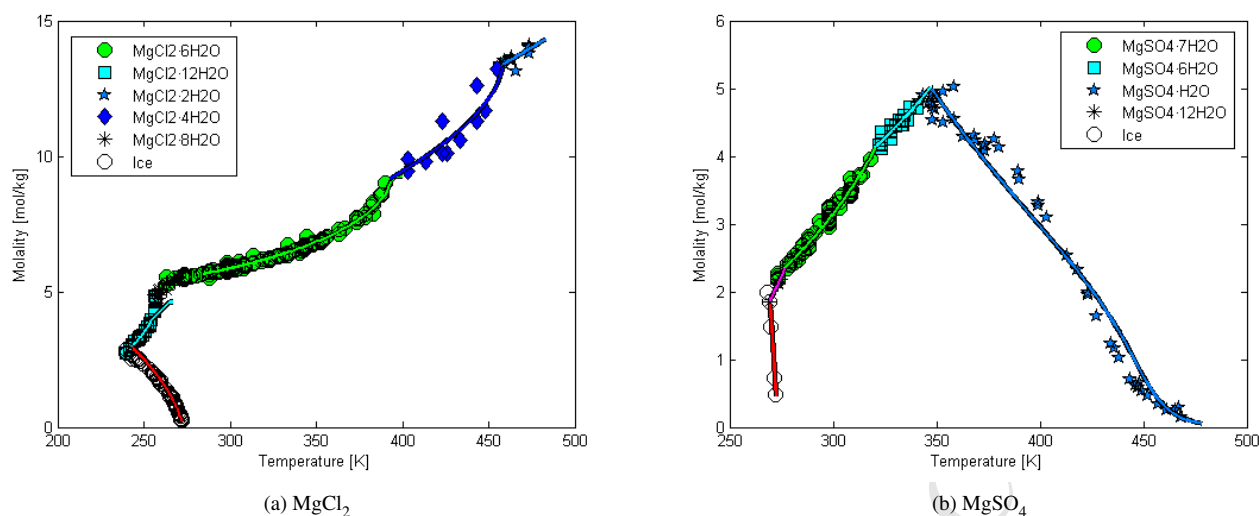


Figure 7: Freezing point depression and salt solubility in water of (a)  $\text{MgCl}_2$  and (b)  $\text{MgSO}_4$ , modelled with the ion-specific parameters of this work.

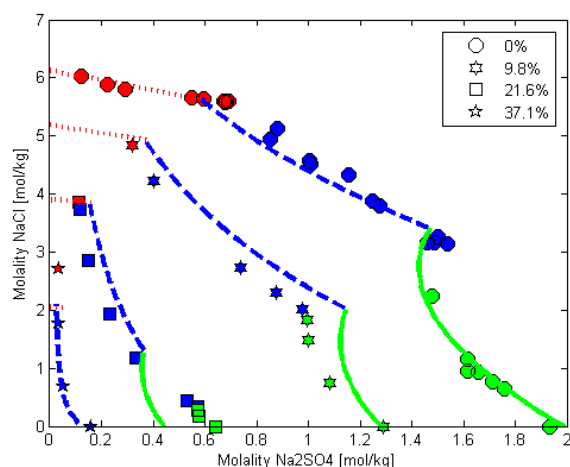


Figure 8: Salt solubility of  $\text{NaCl}$ - $\text{Na}_2\text{SO}_4$  in water-methanol at 298.15 K with different methanol content. The red lines represents  $\text{NaCl}$ , the blue lines  $\text{Na}_2\text{SO}_4$  and the green lines  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ .

#### 4. Conclusions

The eCPA EoS originally presented by Maribo-Mogensen et al. [16], has been shown to work well for a wide range of applications. One drawback of the model is, however, the fact that the model parameters in that work are salt-specific. This has some limitations with regards to salt mixtures as one ion can be part of multiple salts within such a mixture. The aim of this work has been to overcome this limitation by parametrizing the model in an ion-specific approach. By having ion-specific parameters no ion in a solution would be in a situation where the parameter value could come from different salts. In this work it was found that in order to calculate an ion-specific parameter set, some pure component parameters should be adjustable, whereas in the salt-specific approach they were set to literature values or simply set to zero. This new ion-specific parameter set

is determined by estimation to osmotic coefficients and mean ionic activity coefficients in a temperature range from ambient to above 500 K, and the deviations from these properties are compared to those calculated with the salt-specific approach. The model is parametrized for ten cations and seven anions, consisting of alkaline and earth-alkaline cations and halides, sulphate and nitrate being the anions. In the parameter estimation process it was found that for some salts an ion-ion interaction parameter is needed in order for them to work well. On average for all the salts investigated the RAD is found to be 5.1% for mean ionic activity coefficients and 3.7% for osmotic coefficients. These deviations are similar to those found with the salt-specific approach.

The ion-specific parameters have been applied to a series of systems. Mixed salt osmotic coefficients are shown to be accurately predicted for a range of systems containing a diverse selection of the parametrized salts. While most of these systems are low temperature ones, a few also demonstrated accuracy at higher temperatures up to 413.15 K. The model has also been applied to solid-liquid equilibria where single salt solubility can be obtained at high temperatures. This does require adjustment of solid salt standard state properties, however, the system is sensitive and even small changes can make a big difference. As most of the standard state properties for hydrated salts are not available in literature but typically adjusted with other models, adjusting them seems to be a valid approach. The model is also applied to a mixed salt, mixed solvent solubility system, with satisfying results. Finally the model is shown to accurately calculate the effect of salts on the water-methanol VLE.

Overall it has been shown that it is possible to parametrize the eCPA with ion-specific parameters as well as with the salt-specific parameters. Furthermore the ion-specific parameters have proved to work well for a range of applications.

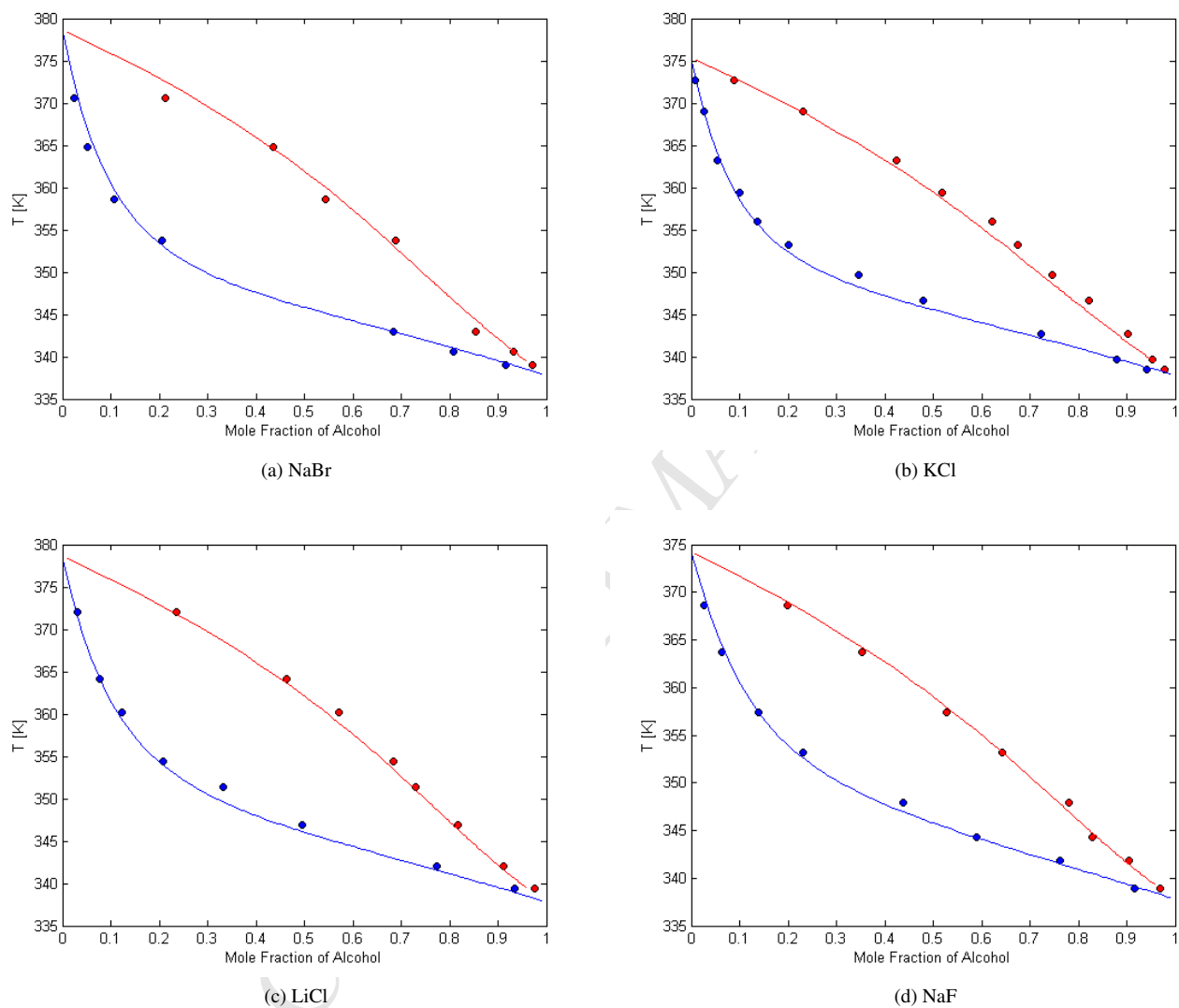


Figure 9: Vapor-liquid equilibrium of water-methanol-salt systems at constant pressure of  $P=101324$  Pa with the salts being: (a) 4 molal NaBr, (b) 2 molal KCl, (c) 4 molal LiCl and (d) 1 molal NaF. The molalities listed are with respect to water and not the mixed solvent, and the mole fraction of methanol given on the x-axis is the salt free mole fraction. Data from [38].

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